Journal of Industrial and Engineering Chemistry 40 (2016) 62–71

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Production of γ-valerolactone from furfural by a single-step process using Sn-Al-Beta zeolites: Optimizing the catalyst acid properties and process conditions

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ARTICLE INFO

Article history:
Received 11 April 2016
Received in revised form 8 June 2016
Accepted 13 June 2016
Available online 20 June 2016

Keywords:
Biomass conversion
Bifunctional catalysis
Sn-Al-Beta zeolites
Furfural
γ-Valerolactone

ABSTRACT

A bifunctional Sn-Al-Beta zeolite which possesses isolated Lewis and Brønsted acid sites was prepared by a post-synthesis procedure and applied to the one-pot conversion of furfural to γ-valerolactone (GVL), a value-added chemical. Sn-Al-Beta was capable of catalyzing a cascade of the transfer hydrogenation and hydrolysis of furfural to GVL by the interplay of Lewis and Brønsted acid sites. The degree of dealumination and the tin-incorporation method largely influence the acid properties of the catalyst and the catalyst selectivity. A high yield of GVL up to 60% was obtained with Sn-Al-Beta 7 (Si/Sn = 63 and Si/Al = 473) at 180 °C in 2-butanol.

Introduction

Research into the catalytic conversion of lignocellulosic biomass into value-added chemicals and fuels has rapidly expanded over the past decade due to the depletion of fossil fuels and concerns about global warming [1,2]. Specifically, the development of cost-effective biomass conversion technologies is critical to compete with fossil fuels. The main components of lignocellulosic biomass are hemicellulose and cellulose, which are sugar polymers. The hydrolysis of biomass allows for the extraction of C5-C6 sugar monomers such as glucose and xylose from the biomass [1]. Although biological processes can directly utilize these C5-C6 carbohydrates for biofuel production, they must be converted further into more reactive intermediates for chemical processes [3]. In this respect, γ-valerolactone (GVL), which can be obtained from C5-C6 sugars via catalytic processing, has recently been identified as a versatile platform molecule for the production of various fuels and chemicals, such as diesel- and jet-fuel-range alkanes, fuel additives, and biopolymer precursors [4,5].

The production of GVL from C5-C6 sugars typically involves a multi-step process, the acid-catalyzed dehydration of sugars to levulinic acid (LA), and the noble-metal catalyzed hydrogenation of LA to GVL with molecular hydrogen (H_2) [4,6]. Furthermore, in the case of C5 sugar, LA production requires additional processing, hydrogenation and hydrolysis, because furfural is the final dehydration product of the C5 sugar [7]. The hydrogenation step of LA and furfural is also an expensive process given its use of precious metal catalysts (e.g., Ru or Pt) and high-pressure H_2 (>30 bar) [6,8]. Therefore, current GVL production technologies are neither efficient nor economic.

In order to reduce the process cost for GVL production, several alternative processes have recently been developed. It has been shown the reduction of LA to GVL can be done through transfer hydrogenation (TH) reactions, such as the Meerwein-Ponndorf-Verley (MPV) reaction, using alcohols as a hydrogen source and inexpensive metal oxides with acid/base properties as a catalyst [9–13]. Among the many types of metal oxide catalysts available, Sn- or Zr-containing beta zeolites has been reported as highly active catalysts for TH reactions of LA and its ester due to their isolated Lewis acid sites and silanol groups adjacent to metal sites, creating separate Lewis acid-base pairs. For instances, Wang et al.

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http://dx.doi.org/10.1016/j.jiec.2016.06.007

reported that the MPV of LA over Zr-Beta zeolite using 2-pentanol as a hydrogen donor results in a high yield of GVL (>96%) [11]. Koehle and Lobo recently showed that Sn- and Zr-Beta zeolites are also active for catalyzing the MPV of furfural to furfuryl alcohol (FA) using 2-propanol as a hydrogen donor [14]. Another study showed that GVL can be produced directly from furfural by combining the MPV reaction step with an acid-catalyzed hydrolysis step. Bui et al. reported the one-pot conversion of furfural to GVL through sequential MPV and hydrolysis reactions using a physical mixture of Zr-Beta zeolite and Al-MFI zeolite with a crystalline nanosheet morphology as catalysts [15]. This one-pot reaction is catalyzed by the interplay of Lewis and Brønsted acid catalysts, in which the Lewis acids provided by Zr-Beta catalyze the MPV reaction and the Brønsted acids provided by Al-MFI catalyze the hydrolysis reaction.

Inspired by these previous reports, we conceived of a one-step process for the conversion of furfural to GVL using a single catalyst featuring Brønsted/Lewis acid properties. Although the physical mixture of Lewis and Brønsted acid zeolites has been shown to be effective for the one-pot conversion of furfural to GVL, it is highly beneficial to use a single catalyst which contains both Brønsted and Lewis acid sites in terms of catalyst reusability and selectivity. In addition, in order to improve the potential of GVL production from C5 sugars, such a bifunctional catalyst system must be developed.

The overall reaction pathway for the one-pot conversion of furfural to GVL is shown in Fig. 1 [15,16]. Catalyzed by Lewis acids, furfural is initially reduced to furfuryl alcohol (FA) via the MPV reaction and is subsequently etherified to furfuryl ether (FE). Next, catalyzed by Brønsted acids, FE is converted to alkyl levulinate (isopropyl levulinate, IPL) through hydrolytic ring-opening reactions. In addition, FE can initially be converted to α- or β-angelica lactone (α- or β-AL) and then undergo hydrolysis and etherification to form alkyl levulinate. Finally, catalyzed by Lewis acids, alkyl levulinate undergoes a MPV reaction and subsequent lactonization to form GVL.

Based on the previous reports of the high activity of Lewis acidic Sn or Zr-Beta zeolite for the MPV reaction and of Brønsted acidic Al-MFI zeolite for the hydrolysis reaction, a zeolite containing both Lewis and Brønsted acid sites can be a suitable choice as a catalyst. However, it is difficult to incorporate both Brønsted acidic Al and Lewis acidic Sn or Zr into the zeolite framework by conventional hydrothermal synthesis due to the extremely slow rate of Sn incorporation [17,18]. Recently, a simple post-synthesis procedure for the preparation of Sn, Al-containing beta was reported. This procedure consists of the partial dealumination of Al-Beta followed by the incorporation of Sn via a solid-state ion-exchange (SSIE) process or grafting [19–24]. Because the partial dealumination of Al-Beta induces the formation of a silanol nest at the site where the Al is removed and leaves some residual Al sites in the framework, the incorporation of tin into the dealuminated beta can produce Sn-Al-Beta zeolite, which has both framework Sn and Al sites [22]. The presence of Lewis and Brønsted acid sites in the prepared Sn-Al-Beta were demonstrated via the conversion of glucose and 1,3-dihydroxyacetone to 5-hydroxymethylfurfural and ethyl lactate, respectively, which involve a combination of Lewis acid-catalyzed isomerization and Brønsted acid-catalyzed dehydration reactions [22,25]. More recently, Antunes et al. reported the combined MPV and dehydrations of furfural to bio-products, including FE, α-AL, and LA, over Sn-Al-Beta or Zr-Al-Beta [16,26]. However, there are no reports which present a systematic study of this bifunctional zeolite for the production of GVL.

The objective of this paper is to study a single catalytic process for the production of GVL from furfural using Sn-Al-Beta zeolites. The effects of the tin-incorporation method and the degree of Al removal on the acid site distribution of Sn-Al-Beta and the GVL selectivity were investigated to optimize the catalytic properties toward the production of GVL. Solid-state ion-exchange (SSIE) was employed for tin incorporation, and the level of Al removal was adjusted by varying the acid concentration during the dealumination step. Al-free Sn-Beta was also prepared by a hydrothermal synthesis method and the activity of the physical mixture of Sn-Beta and Al-Beta was compared with those of Sn-Al-Beta zeolites to understand how the proximity of active sites affects the catalytic chemistry. In addition, the effects of the reaction conditions, including the temperature, the hydrogen donor, and the reaction times, were investigated to optimize the GVL yield.

Experimental

Material preparation

Al-Beta zeolite (Zeolyst CP814E, $SiO_2/Al_2O_3 = 25$) was used to prepare dealuminated beta zeolites following the similar procedure to previous works [24]. For dealumination step, desired amount of Al-Beta zeolite ($SiO_2/Al_2O_3 = 25$) was mixed with appropriate amount of HNO_3 solution (1.5 M, 3 M, 7 M, and 14 M) with a ratio of 20 ml solution per 1 g of zeolite and heated up to 80 °C for 24 h. At the end of dealumination process suspended

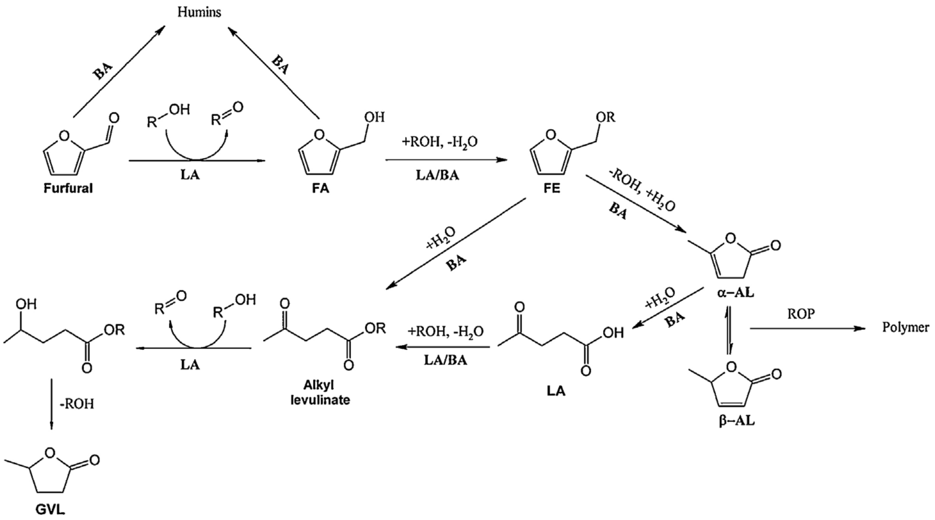

Fig. 1. Reaction networks for the one-pot conversion of furfural to GVL (BA: Brønsted acid, LA: Lewis acid, FA: furfuryl alcohol, FE: furfuryl ether, α- or β-AL: α- or β-angelica lactones, ROP: ring opening polymerization) [15,16].